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Catalytically Active Sites on Ni₅P₄ for Efficient Hydrogen Evolution Reaction From Atomic Scale Calculation

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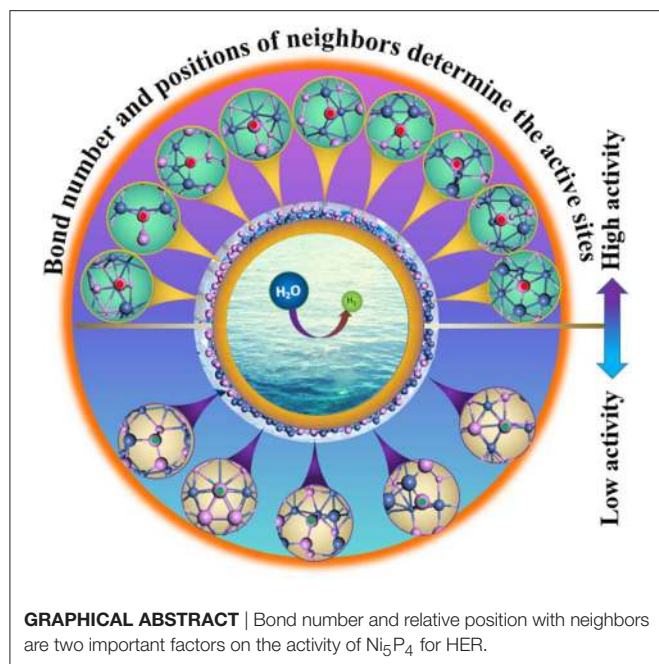
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Ni₅P₄ has received considerable attention recently as a potentially viable substitute for Pt as the cathode material for catalytic water splitting. The current investigation focuses on theoretical understandings of the characteristics of active sites toward water splitting using first-principle calculations. The results indicate that the activity of bridge NiNi sites is highly related on the bond number with neighbors. If the total bond number of NiNi is higher than 14, the sites will exhibit excellent HER performance. For the top P sites, the activity is greatly affected by the position of coplanar atoms besides the bond number. Data of bond length with neighbors can be used to predict the activity of P sites as reviewed by machine learning. Partial density of state (PDOS) analysis of different P sites illustrates that the activity of P sites should form the appropriate bond to localize some 3p orbitals of the P atoms. Bond number and position of neighbors are two key parameters for the prediction of the HER activity. Based on the current work, most of the low-energy surfaces of Ni₅P₄ are active, indicating a good potential of this materials for hydrogen evolution reactions.

Keywords: nickel phosphides, water splitting, hydrogen evolution reaction, density functional theory, machine learning

INTRODUCTION

Growing concerns on the energy crisis and environmental problems urgently demand for the development of clean and affordable renewable energy sources as feasible alternatives to the diminishing fossil fuels. Water electrolysis is the most promising option to generate high purity hydrogen as a clean energy source, but unfortunately, the required cathode materials for electrochemical water splitting, such as Pt, is too expensive for large-scale application (Li et al., 2016). This has prompted continued research effort toward searching for earth-abundant elements as the cathode materials for large-scale applications. The potential candidates include transition metals (McKone et al., 2013), and their dichalcogenides (Chen et al., 2011; Voiry et al., 2013; Xie et al., 2013; Yang et al., 2013), carbides (Chen et al., 2013a,b), borides (Vrubel and Hu, 2012), nitrides (Cao et al., 2013), phosphides (Feng et al., 2016), and metal-free carbon nitrides (Merlet et al., 2012; Meng et al., 2017), etc.



Among these materials, nickel phosphides (Ni_xP_y) have shown great promise due to their high activity and stability (Gerasimov and Simirskii, 2008; Laursen et al., 2018). Ni_xP_y has been reported in more than 10 stoichiometric compositions (Feng et al., 2014; Huang et al., 2014; García-Muelas et al., 2018). Among them, Ni₅P₄ has drawn lots of attentions recently on its synthesis, structure, and reactivity (Shu et al., 2005; Zhao et al., 2015). For example, Pan et al. investigated the electrocatalytic property for hydrogen evolution reaction (HER) of Ni₁₂P₅, Ni₂P, and Ni₅P₄, and found that the catalytic property followed the order of Ni₅P₄ > Ni₂P > Ni₁₂P₅ (Pan et al., 2015). Laursen et al. found that the Tafel slope and overpotential at -100 mA cm^{-2} are 33 mV dec^{-1} and -62 mV in $1 \text{ M H}_2\text{SO}_4$, which are very close to Pt in strong acidic solution (Laursen et al., 2015). Although Ni₅P₄ has high activity for HER, an atomic-scale understanding of their reactivity has been elusive, because of the diversity of possible active sites on its different crystal surfaces. While experimental approaches will face a great challenge, theoretical studies can provide insight of the active sites and therefore become an important tool for understanding the catalytic activity of Ni₅P₄.

Some researchers believed that the superior performance of Ni₅P₄ can be attributed to a high positive charge on Ni atoms and the ensemble effect of P, where the number of Ni3-hollow sites that bind H very strongly is decreased due to the abundance of P, which therefore leads to more thermoneutral adsorption (Liu and Rodriguez, 2005; Liu et al., 2005). However, recent experimental research indicates that NiP₂ material is also able to exhibit excellent HER activity although there are no Ni3-hollow sites on the surfaces due to the enriched P atoms, as shown in **Figure S1** (Jiang et al., 2014; Pu et al., 2017). Recently, Wexler et al. found through simulation that P site was the most active site, but the hollow Ni sites on Ni₂P and

Ni₅P₄ (0001) surfaces were not active (Wexler et al., 2017). This result agrees with Jin et al. and our recent work, where we found P sites were suitable for HER for Ni₃P (Jin et al., 2016; Hu et al., 2018a). However, it was also found not all P sites are active. Therefore, it is necessary to obtain a fundamental understanding of the activity for P sites from the atomic scale, which are important for the development of a broad range of catalytic materials. Till now, no such model exists to reveal an in-depth understanding of the catalytically active sites. Therefore, finding the key parameters affecting the HER activity becomes an essential task for the rational design and optimization of efficient catalysts.

Herein, we report a comprehensive theoretical study on the atomic active sites of Ni₅P₄ for HER. It was found that there are three types of active sites, namely the bridge NiNi sites, bridge NiP sites, and top P sites. The activity of these active sites is closely associated with the bond number and position with respect to the neighbors. A direct link between the macroscopic activity and the atomic-scale properties was therefore established by regression and machine learning method based on the generated understandings. The outcome provides not only an improved understanding of Ni₅P₄, but also a guideline for the design and synthesis of this material as an electrocatalyst for HER.

COMPUTATIONAL METHODS

All calculations were implemented in the CASTEP module of the Materials Studio package (Accelrys Inc., San Diego, CA, USA). During the calculations, self-consistent periodic DFT was adopted by generalized gradient approximation with Perdew-Burke-Ernzerhof exchange-correlation functional. The plane-wave ultrasoft pseudopotential method, describing the ionic cores of Ni- $3d^8 4s^2$ and P- $3s^3 3p^2$, were represented the electron-ion interaction in reciprocal space. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme was selected as the minimization algorithm. The energy cutoff is 380 eV and the SCF tolerance is $5.0 \times 10^{-7} \text{ eV atom}^{-1}$. The k-points samplings is set as $1 \times 1 \times 1$ for different surfaces. The optimization is completed when the energy, maximum force, maximum stress and maximum displacement are smaller than $5.0 \times 10^{-6} \text{ eV atom}^{-1}$, 0.01 eV \AA^{-1} , 0.02 GPa , and $5.0 \times 10^{-4} \text{ \AA}$, respectively. These parameters were verified by experimental data, as listed in **Table S1** and **Figure S2**, and our previous calculations (Hu et al., 2018a).

The surfaces, containing at least six layers, were obtained from the bulk Ni₅P₄ (space group *hP36*, 186, as shown in **Figure S3**) with a vacuum region of 15 \AA . Considering the symmetry of bulk Ni₅P₄, seven low-index surfaces, viz., the (001), (100), (110), ($\bar{1}\bar{1}0$), (101), (111), and ($1\bar{1}\bar{1}$), with different terminations were chosen during calculation. Different terminations are indicated using capital letters A, B, C, D, and E (more information can be found in **Figures S4, S5**). It was found that only P-rich and stoichiometric surfaces are stable in all low-index surfaces (**Figure S6**). Based on the surface energies, seven low energy surfaces (details in **Figure S7**) are selected for the investigation

of the catalytic activity. The energies of species related to the calculation can be found in **Table S2**.

The Gibbs free energy of adsorption hydrogen atom is calculated by Equation (1) (Hu et al., 2018b):

$$\Delta G_H = E[\text{Ni}_5\text{P}_4 + \text{H}] - E[\text{Ni}_5\text{P}_4] - 1/2E[\text{H}_2] + \Delta E_{\text{ZPE}} - T\Delta S_H \quad (1)$$

where $E[\text{Ni}_5\text{P}_4 + \text{H}]$ is the total energy of the system, including the adsorbed molecules and the Ni₅P₄ facet; $E[\text{Ni}_5\text{P}_4]$ is the energy of Ni₅P₄ facet; $E(\text{H}_2)$ represents the total energy of a gas phase H₂ molecule; ΔE_{ZPE} denotes the zero-point energy of the system simplified as 0.05 eV. The term $-T\Delta S_H$ is the contribution from entropy at temperature K, taken as 0.20 eV at 298 K (Tang and Jiang, 2016).

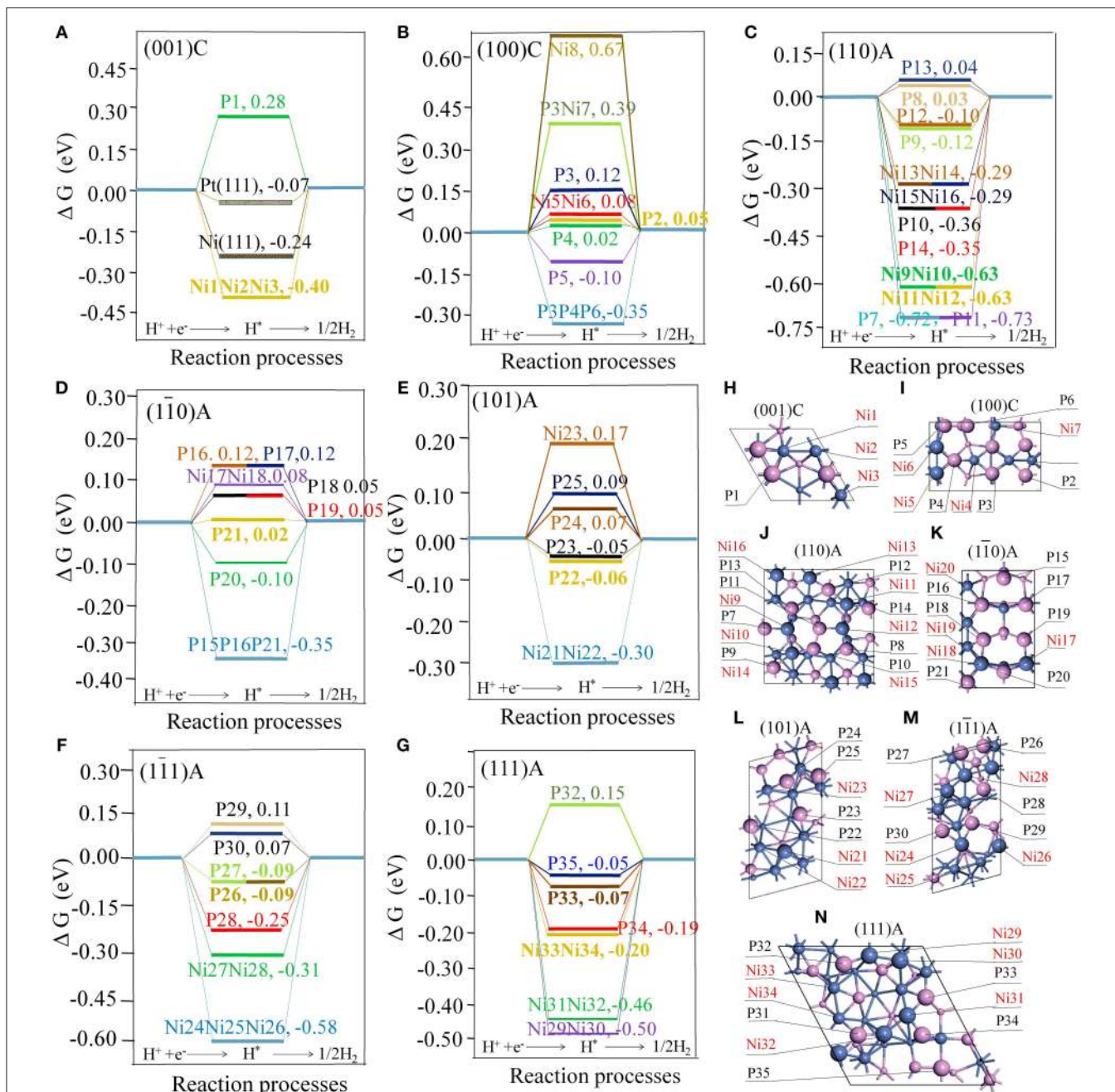


FIGURE 1 | Free energy profile of H₂ generation on different active site of surfaces with the units in eV (A) the (001)C surface, with Pt(111) and Ni(111) surfaces included for comparison; (B) the (100)C surface; (C) the (110)A surface; (D) the (110)A surface; (E) the (101)A surface; (F) the (111)A surface; (G) the (111)A surface. The geometry structures of different surfaces (H) the (001)C surface (I) the (100)C surface; (J) the (110)A surface; (K) the (110)A surface; (L) the (101)A surface; (M) the (111)A surface; (N) the (111)A surface; Violet spheres stand for P atoms and blue spheres stand for Ni atoms. Large, medium, and small spheres stand for the atoms located in the first, second, and third layer.

RESULTS AND DISCUSSION

Active Sites for HER

ΔG_H is considered as a good descriptor of materials for catalyzing hydrogen generation following either the Volmer-Tafel or the Heyrovsky mechanism (Hinnemann et al., 2005). In principle, smaller of $|\Delta G_H|$ means better HER activity (Zheng et al., 2014). **Figure 1** displays details of the adsorption energies involved in the water splitting process on the different sites.

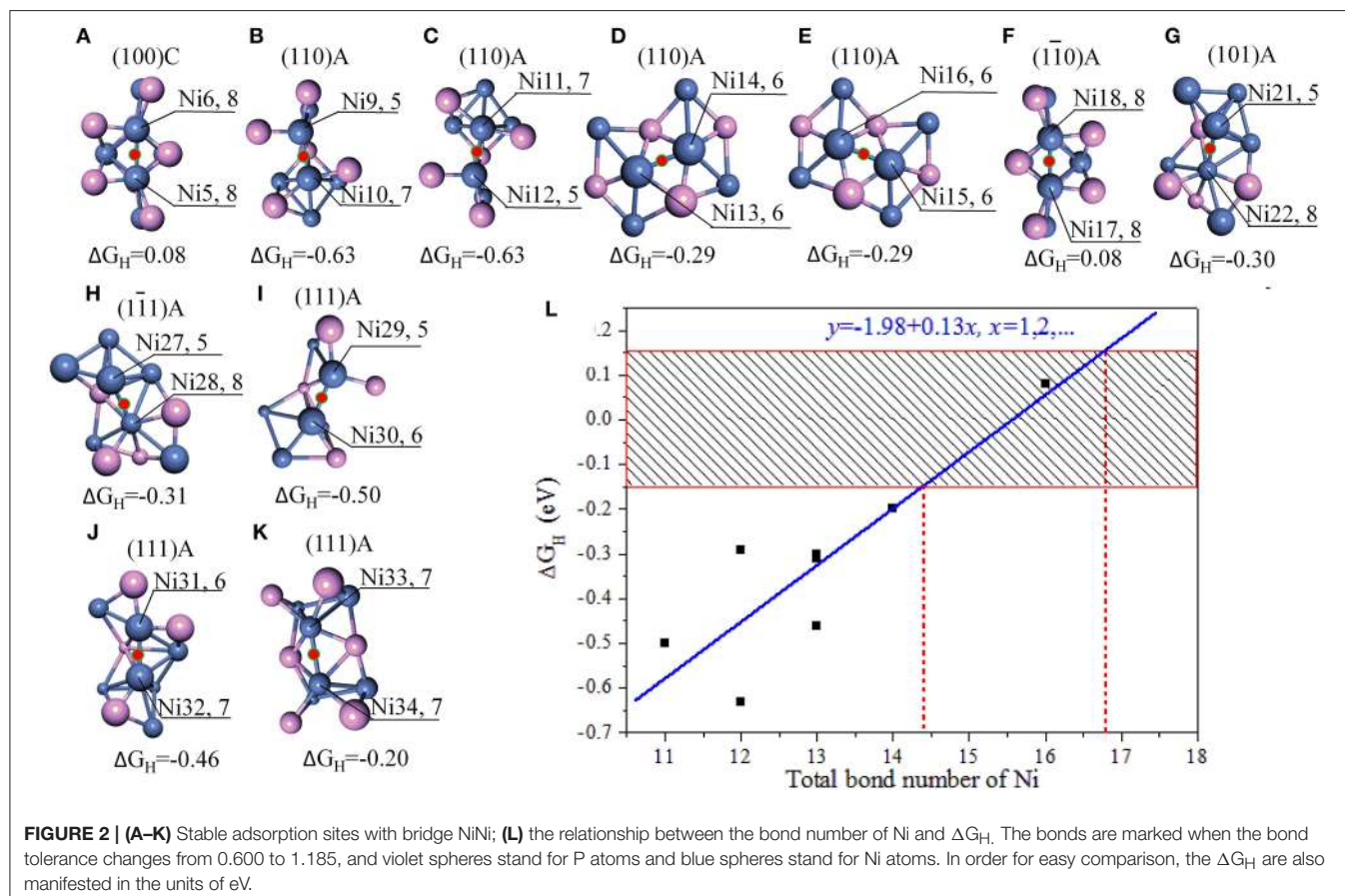
As illustrated in **Figure 1H**, we found that ΔG_H for Ni(111) and Pt(111) surfaces are -0.23 and -0.07 eV, respectively. This is largely consistent with previous experimental and calculated results (Nørskov et al., 2005; Tan et al., 2013). As seen from **Figure 1**, some hollow NiNiNi sites, hollow PPP sites, bridge NiNi sites, and top P sites are able to stably adsorb the hydrogen atom (H^*). If we consider a site is active when the $|\Delta G_H|$ is smaller than 0.15 eV, the hollow sites are not catalytically active while some bridge NiNi sites and top P sites may be active. In order to reveal the characteristic of the active sites, detailed structures for bridge NiNi sites and top P sites are illustrated in **Figures 2, 3**.

As indicated in **Figures 2A–K**, only a few bridge NiNi sites are active, such as the bridge Ni5Ni6 and Ni17Ni18 while others are not. It is notable the linear correlation coefficient is 0.869 between total bond number of Ni and ΔG_H , and the linear fit

between bond number of Ni (x) and ΔG_H (y) obeys $y = -1.98 + 0.13x$. Therefore, the bond number plays an important role to the activity and it may exhibit excellent HER performance when the total bond number of Ni equals to 15 or 16 (**Figure 2L**).

Furthermore, it is interesting to notice that the ΔG_H for most top P sites are closer to zero (P2, P3, P4, P5, P8, P9, P12, P13, P16, P17, P18, P19, P20, P21, P22, P23, P24, P25, P26, P27, P29, P30, P33, and P35). It means these sites are able to trap protons and bond the atomic hydrogen while still able to desorb H_2 easily. This finding agrees well with the results reported by Jin et al., where it was reported that top P may be the active sites for Ni₃P (Jin et al., 2016). Additionally, other top P sites are not suitable for HER such as P1, P7, P10, P11, P14, P28, P32, and P34. In order to clearly recognize the key parameters affecting the activity, more detailed geometry structures of P sites are plotted in **Figure 3**.

As indicated in **Figure 3**, P sites can be divided into three types based on the number of PP bond during the surface cleavage. The first type is the one that has two PP bonds, these P sites are active if one of the PP bond is a double bond (P35, P5, and P20) while the other is not (P7, P11, and P1). The second type is the P sites with 1 PP bond. All such P sites have three bond number with Ni. These P sites are active if only one neighboring atom (regardless of Ni or P atom) is coplanar with this P site (P2, P18, P19, P29, P30, P33, P22, P23, P26, and P27). While the P



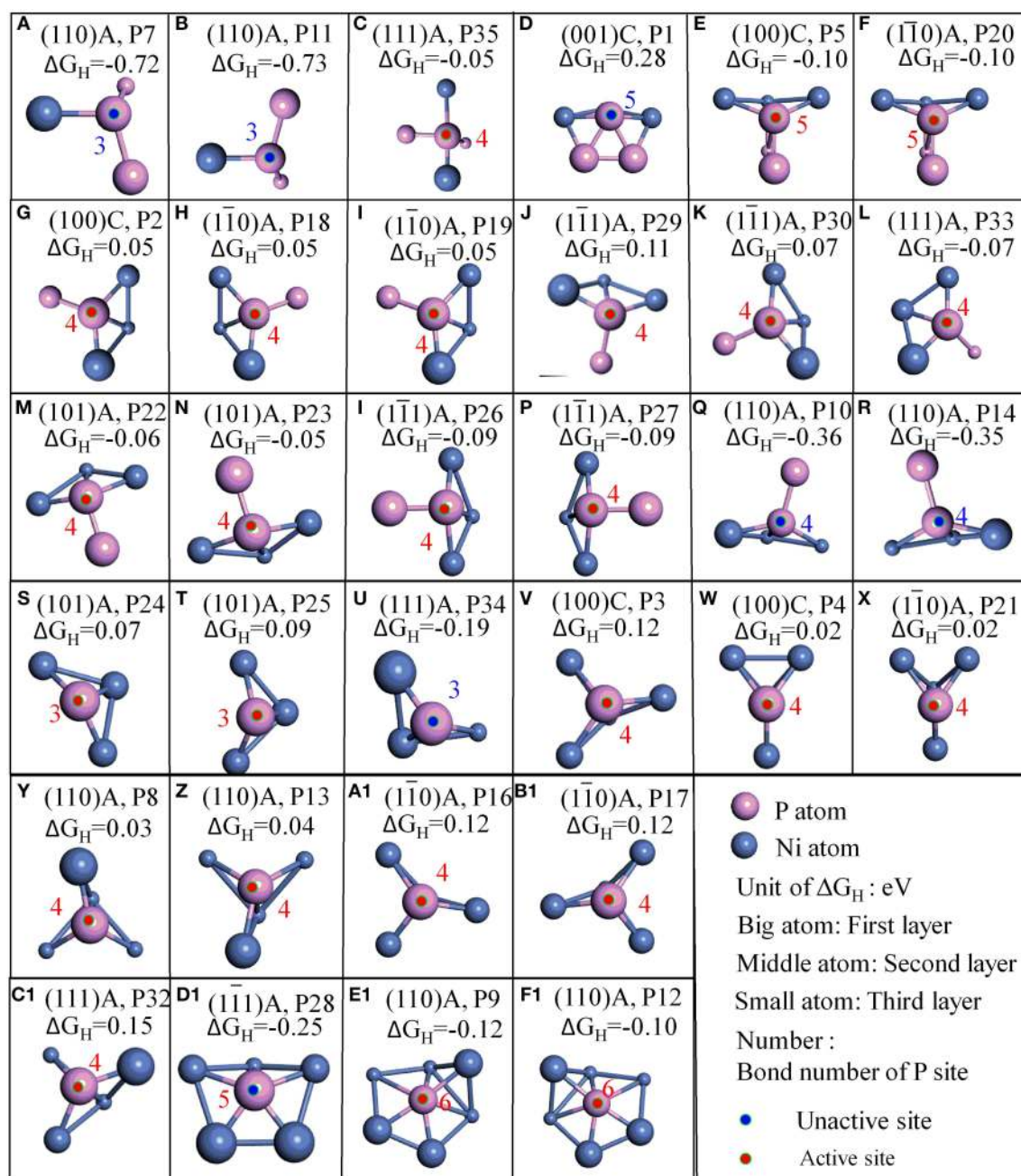
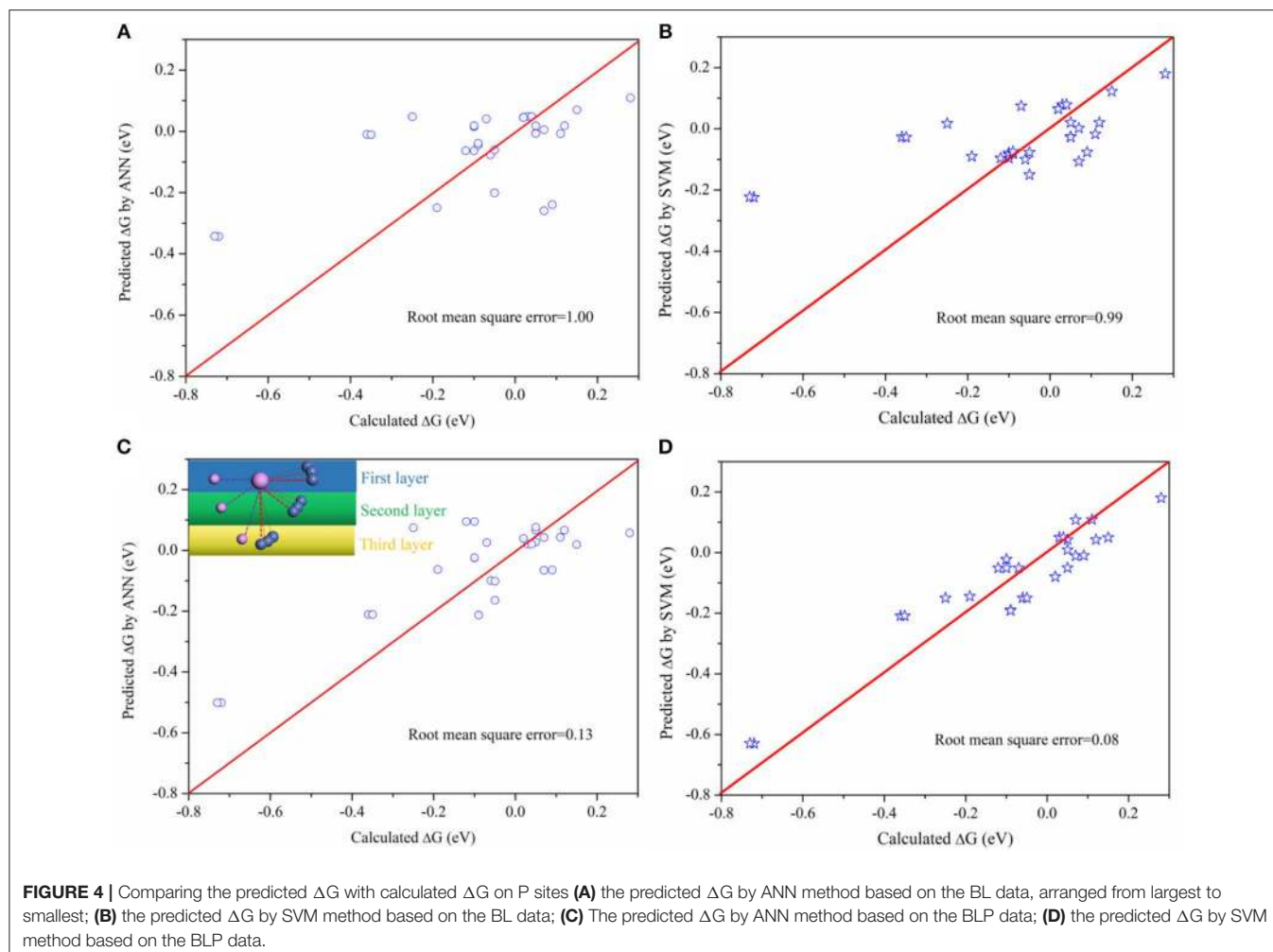


FIGURE 3 | Stable adsorption sites with surface P atoms (**A–F**) surface P sites with 2 PP bonds; (**G–R**) surface P sites with 1 PP bonds; (**S–F1**) surface P sites with 0 PP bonds; The bond number (red number) of P are marked when the bond tolerance changes from 0.600 to 1.185.

sites are not active if the two neighboring atoms are coplanar with the P site. For example, P10 and P14 are coplanar with one neighboring Ni and one neighboring P. The third is the P site without PP bond. This type of P sites have 3, 4, 5, and 6 bond number with Ni. For the P sites with three bond number, the P sites are active if no neighboring atom is coplanar with this P site (P24, P25), while it is not active if one neighboring atom is coplanar with this P site (P34). Furthermore, P sites

with four or six bond number are active while P sites with five bond number are not active. The information thus displays a “structure sensitivity” of this material. The determination of the bond number on the activity has also been found in other catalysts (Zhao et al., 2016; Wang et al., 2018). In this work, not only the bond number but also the relative position with neighbors play an important role to determine the activity of P atom for HER (**Graphical Abstract**).



Although this connection between activity and bond property is obvious, it is difficult to fit by mathematical models due to the complexity. Machine learning method, which is capable of analyzing complex data, is used to analyze the results obtained. Two machine learning methods, the Artificial Neural Network (ANN) and Support Vector Machine (SVM), were used to predict the activity. During the ANN training, the number of input layer, middle layer, and output layer were chosen based on the characteristics of the data. This data were randomly split into training (50%) and testing (50%) groups to prevent overtraining. For the SVM model, the regularization parameter is set as 10 in order to balance the classification accuracy and overfitting for the training data. The Kernel type is Radial Basis Function (RBF) with RBF gamma equals to 0.1. Furthermore, the model will stop the optimization when the error between the adjacent steps is $<0.1\%$. The results are shown in **Figure 4**. There are two database during the training, one for the bond length (BL) (**Table S3**), where the bond length of active sites are arranged from long to short, and the other the bond length–position (BLP) (**Table S4**), arranged from the first, second, and third layer based on position of active P site as indicated in the inset image of **Figure 4C**.

As indicated in **Figure 4**, there is a larger root mean square error based on BL data while the error will be greatly reduced based on BLP data. The different between BLP and BL data is only whether the data contains the information of relative positions or not. The result verifies our early finding (**Figure 3**) that the positions of neighboring atoms indeed play an important role on the catalytic activity. Furthermore, The SVM model is more appropriate for the catalytic activity prediction than the ANN model. Therefore, this work demonstrates that it is possible to establish a relationship between activity (macroscopic activity) of P sites and their bond length (an atomic-scale property) by using appropriate machine learning method. This method is potentially useful for high-throughput calculations because it can drastically reduce the amount of calculations.

Electronic Characteristics of Active Sites

As indicated above, most of P sites are active sites in Ni₅P₄. To reveal the origin of HER activity, partial density of states (PDOS) of different P sites are illustrated in **Figure 5**.

Comparing the PDOS of different sites (**Figure 5A** and **Figure S8**), we found the separated $3p$ orbitals, one localized

for electrochemical water splitting. The results indicate the bond number and relative position with neighbors play an important role on the activity of Ni₅P₄ for HER. There are two active sites, namely the bridge NiNi sites and top P sites. The bridge NiNi sites with a total bond number of Ni equals to 15 or 16 exhibit good HER performance. For the top P sites, the activity is greatly affected by bond number of P as well as the coplanar atoms. Data on the bond length with neighbors can be used to predict the activity of P sites as reviewed by machine learning. PDOS of different P sites illustrates that the activity of P sites should form the appropriate bond to localize some 3p orbits of P atom. Weakly bonded or strongly bonded P atom will weaken its activity. Therefore, bond number and positions of neighbors are two key parameters for HER activity of Ni₅P₄ material. The current work establishes a clear connection between the macroscopic activity and geometrical structures of Ni₅P₄ material. The outcome not only provides important insights into the surface activity for water splitting, but also opens up an exciting opportunity to quickly design and optimize the materials with high catalytic activity. Except the (001)C that is non-active, most of the investigated surfaces of Ni₅P₄, e.g., the (100)C, (110)A, (1 $\bar{1}$ 0)A, (101)A, are active for HER, indicating that this material is a good candidate for practical hydrogen production.

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DATA AVAILABILITY

The raw data supporting the conclusions of this manuscript will be made available by the authors, without undue reservation, to any qualified researcher.

AUTHOR CONTRIBUTIONS

JH and ZC conceived and designed the calculations. XC, WC, and YD performed the calculations. XZ and GL analyzed the data. JH and ZC revised the paper.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2019.00444/full#supplementary-material>

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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